Comment on *Structure and Hyperfine Parameters of E'_1 Centers in $\alpha-$quartz and Vitreous SiO_2*

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Boero *et al.* have recently proposed [1] a model for the E′ center in quartz and silica, based on ab initio studies of the singly positive charge state of the oxygen vacancy V_O. They find that in the +1 charge state, V_O undergoes a distortion to a puckered configuration whose calculated hyperfine activity is consistent with the observed data. The purpose of this Comment is to point out that recent ab initio density-functional calculations on the oxygen vacancy in $\alpha-$quartz [2] rule out the possibility of identifying the +1 charge state of the vacancy with the E′ center as suggested in [1]. Our results [2] indicate the $Q = -3$ charge state of V_O as another possible candidate.

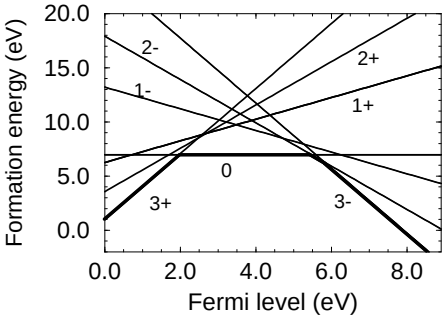

FIG. 1. Calculated formation energies for the various charge states of the oxygen vacancy in $\alpha-$quartz.

The formation energies of the oxygen vacancy are displayed in Fig.1 as a function of the Fermi level (whose zero is chosen at the valence band top). The oxygen vacancy is a negative-U center whose ground state can have the charge states Q=[+3,0,–2,–3]. The singly charged states, in particular the +1 state, are never stable against capture or release of further electrons. Therefore the singly positive vacancy cannot be invoked as a candidate E′ center. This remains true accounting for the puckering energy gain of 0.3 eV [1].

Our calculations are technically quite comparable to those in [1]. We studied a single oxygen vacancy in 36-atom $\alpha-$quartz supercells using conjugate-gradient total energy minimization with ultrasoft pseudopotentials [3], a plane-waves basis cut off at 20 Ryd, and one special k-point. No symmetry restriction is imposed, and all geometries are fully relaxed. The theoretical lattice constants (deviating less than 1% from experiment) are used. The energy zeroes in the charged supercells are carefully aligned [4].

The $Q = -3$ state of V_O is characterized by a major lattice distortion involving three vacancy-neighboring tetrahedral units (Fig.2). While the $Q = 0$ and $Q = +3$ states fail to match most of the magnetic or optical properties of the E′ center, the $Q = -3$ state satisfies most requirements for identification with E′. Calculated optical transition energies agree well with absorption and emission bands commonly associated with E′. The main feature of the charge density of the unpaired electron in the defect state (not shown due to space constraints) is a pronounced lobe associated with atom Si_3 (see Fig.2), and pointing approximately towards Si_1. The angle formed by this dangling lobe with the neighboring O atoms is $\sim 100^\circ$ in accordance with experimental estimates. Two additional, weaker density features are associated with Si_1 and Si_2. The overall picture seems compatible with the observation of one strong, and two weak hyperfine signals. Calculated hyperfine parameters are unfortunately not available at the moment.

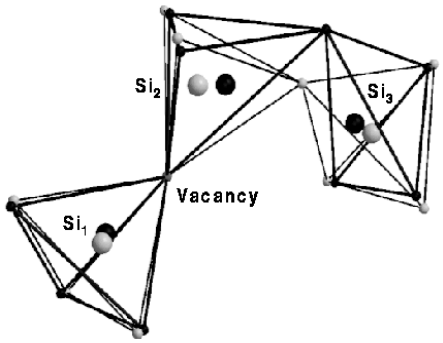

FIG. 2. Equilibrium configuration of V_O for $Q = -3$ (thick lines, black atoms) and $Q = 0$ (thin lines, grey atoms).

In summary the +1 state of the oxygen vacancy in quartz cannot be associated with the E′ center. An alternative candidate is the –3 charge state of the same center.

[1] M. Boero, A. Pasquarello, J. Sarnthein, and R. Car, Phys. Rev. Lett. **78**, 887 (1997)
[2] C. M. Carbonaro, V. Fiorentini and S. Massidda, to be published.
[3] R.D. King-Smith and D. Vanderbilt, Phys. Rev. B **49**, 5828 (1994).
[4] V. Fiorentini, F. Bernardini, A. Bosin and D. Vanderbilt, in *The Physics of Semiconductors*, M. Scheffler and R. Zimmermann eds. (World Scientific, Singapore 1996), p. 2881.